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Degradation of Nicotine in Chlorinated Water: Pathways and Kinetics



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Degradation of Nicotine in Chlorinated Water: Pathways and Kinetics

U. S. Environmental Protection Agency

Cincinnati, Ohio 45268

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List of Abbreviations

- DPD N, N-diethyl-p-phenylenediamine
- EPA Environmental Protection Agency
- GC/MS Gas chromatography/Mass Spectrometry
- IC Ion Chromatography
- R² Regression coefficient
- UV Ultraviolet

Executive Summary

Nicotine was used as a target compound to evaluate the degradation of alkaloid pesticides in chlorinated drinking water. Nicotine was found to degrade rapidly in the presence of free chlorine. Data from this study was used to determine rate constants and rate coefficients for nicotine under varying experimental conditions.

A series of bench-scale kinetic tests were conducted to determine the fate of nicotine in chlorinated water. The tests were performed using deionized water and chlorinated tap water, various concentrations of nicotine and free chlorine, and at various pH levels. In both types of water, a two-stage reaction was observed—a rapid initial stage followed by a slower second stage. The rapid initial stage followed first-order reaction kinetics, with a rate constant of 0.0067 sec⁻¹ for deionized water and 0.013 sec⁻¹ for tap water. The slower stage followed second-order kinetics for deionized water, with a rate constant of 18 M⁻¹ sec⁻¹. Tap water did not follow second-order kinetics, and the reaction order was qualitatively estimated as first-order with a rate constant of $1.6 \times 10^{-4} \text{ sec}^{-1}$, two orders of magnitude lower than the rapid initial stage. The study found pH to be very stable during each test.

Introduction

Interest in the toxic effects of chemical compounds that are listed in the Chemicals of Environmental Protection Agency Interest, which might be introduced into drinking water, has been elevated due to the threat of terrorist attacks. Because of inherent dilution factors, rivers, lakes, and reservoirs are the least likely potential targets. The quantities of toxic chemicals needed to sufficiently poison drinking water in a reservoir would be logistically impractical. The area of most concern is therefore within water distribution systems.

Of particular interest are the effects of chlorinated drinking water on pesticides. Prior pesticide studies have shown that chlorpyrifos (Duirk and Collette, 2006), diazinon (Zhang and Pehkonen, 1999), aldicarb (Miles, 1991), carbamate (Mason et al., 1990), phorate (Hong and Pehkonen, 1998), thiobencarb (Magara et al., 1994), and carbaryl (Miles et al., 1988) degrade in the presence of chlorinated water. However, these studies were conducted using deionized water. Further, in many cases, the deionized water was spiked with chlorine to levels that were above the U.S. Environmental Protection Agency's (EPA's) maximum contaminant level (MCL) of 4 mg/L (USEPA, 2006). A review article (Wolfe, 1980) cites half-life determinations for pesticides that were conducted in river and pond waters; however, there were no studies cited that examined finished drinking water. Data on the persistence of pesticides in drinking water is limited.

Nicotine is an alkaloid compound, and a pesticide. Alkaloids are nitrogenous bases (usually heterocyclic) widely found in plants. Nicotine formerly found wide use as a pesticide against sucking insects on plants and against lice and mites in chicken coops. (PMEP, 1985) Nicotine [CASRN 54-11-5], with the chemical formula C₁₀H₁₄N₂, consists of a pyridine ring bonded to a pyrrolidine ring, as presented in Figure 1.

Figure 1: Structure of nicotine

The degradation of nicotine in water has been studied, but under severe oxidizing conditions (Zaafarany, 2010). In this study described here, nicotine is subjected to typical drinking water chlorination conditions to evaluate how it degrades. The objective of the study is to illustrate how drinking water would affect alkaloid pesticides, and to address the issue by (a) investigating the fate of nicotine in chlorinated drinking water and deionized water, (b) determining the reaction rate and pathway of the reaction between nicotine and aqueous

chlorine, (c) identifying nicotine's degradation products, and (d) providing data that can be used to assess the potential threat from nicotine in drinking water.

Experimental Procedure

Materials

Nicotine stock solution with a reagent purity of 99.5% was purchased from Chem Service (West Chester, PA). Second source nicotine standards were prepared from a solution obtained from Sigma Aldrich (St. Louis, MO). Deionized water was buffered to pH 7 using anhydrous sodium dihydrogen phosphate (Sigma, ACS reagent grade) and anhydrous disodium hydrogen phosphate (Fisher, Pittsburg, PA; ACS reagent grade). The pH standards used were pH 4, pH 7, and pH 10 (Fisher Certified). The chlorine source was derived from a 10-13% reagent grade sodium hypochlorite solution (Ulrich Chemical Inc., Indianapolis, IN). The free chlorine standards (25-30 mg/L Cl₂) were purchased from Hach (Hach Company, Loveland CO).

The deionized water used in the study was produced by passing moderate-quality deionized water through a Barnstead[™] Nanopure[®] water purification system (Thermo Scientific, Waltham, MA) equipped with pretreatment carbon filtration, cation exchange filtration, mixed cation/anion exchange filtration, and a final carbon/ion exchange filtration.

The drinking water used in the study was chlorinated Cincinnati tap water. Before sampling, the tap water was allowed to flow from the faucet for approximately 15 minutes. After this flush, the chlorine concentration was checked over the course of several minutes; sampling commenced after a stable chlorine level was achieved.

Deionized water was buffered to pH 7 using a buffer made from sodium dihydrogen phosphate and disodium hydrogen phosphate. Fresh buffer solution was prepared once a week during the experiments. No pH adjustment was made to tap water.

Methods

Tap water was dechlorinated by aeration for 5 days prior to each experiment. Free chlorine in the water was monitored to verify effective chlorine loss. Water with a free chlorine concentration of less than 0.10 mg/L was deemed suitable for use as dechlorinated water, or as a starting point for rechlorination.

All experiments were conducted in a laboratory held at a temperature of $20 \pm 2^{\circ}$ C.

Nicotine was spiked into the appropriate test water by adding a known amount of neat nicotine to 2 liters of test water contained in a 10-L glass carboy. In a separate 4-L beaker, a known amount of sodium hypochlorite solution was added to 2 liters of water. These solutions were assayed for nicotine or chlorine prior to use. Free chlorine analysis was conducted immediately

after sampling. Once the free chlorine level was confirmed, the newly chlorinated water was added to the nicotine solution in the carboy. The reaction mixture was mixed by swirling for approximately 25 seconds. The zero-time sample was collected immediately after mixing. The carboy was then covered with foil and the mixture stirred continuously during the remainder of the experiment using a magnetic stir bar and stir plate. Additional samples were collected at designated time intervals. These samples were tested immediately for free chlorine and pH, followed by ion chromatography (IC) analysis for nicotine. The aliquot used for nicotine analysis was immediately quenched with the required amount of sodium thiosulfate (5% solution) to destroy the chlorine.

Nicotine and free chlorine concentrations, as well as pH, were critical parameters for this study. The concentration of nicotine was determined using an IC method developed by (Ayers et al., 1998). Ayers et al. reported a sensitive and rapid (10 minutes per analysis) method for determination of aqueous nicotine employing solvent gradient elution with ultraviolet (UV) detection. The method was found to be linear in response over the concentration range investigated (0.5-512 μ M, 0.081-83 mg/L) and has a limit of detection of (~0.01 μ M, ~2 μ g/L) for a 50 μ L injection. Our laboratory analyzed 10 microliters of sample.

This study also employed GC/MS to analyze some nicotine samples, followed by a library search to identify intermediate compounds and by-products of the nicotine reaction with chlorine. These samples were extracted by a modified EPA Method 507 (Engels and Graves, 1989).

The Hach[®] Pocket Colorimeter[™] kit used for free chlorine analysis was set at a wavelength of 530 nm. A Hach SwifTest[™] dispenser was used to introduce N, N-diethyl-p-phenylenediamine (DPD) directly into the water samples. DPD reacts with hypochlorous acid and/or hypochlorite ion to form a pink color; the intensity of the color is proportional to the free chlorine concentration (Hach, 2005; Harp, 2002). This method is accurate from 0.02 to 2.00 milligrams per liter (mg/L). When determining free chlorine concentrations that were above the analytical range, samples were diluted with the appropriate amount of deionized water to bring the final concentration into the analytical range. The samples were analyzed immediately after dilution.

Measurements of the pH were conducted using a Thermo Orion 720 pH Meter (Thermo Scientific). A three-point calibration was conducted daily, prior to pH measurement, using pH standards at pH 4, 7, and 10.

A Mettler[™] Research Electronic Balance (AE200; Mettler-Toledo, LLC, Columbus, OH) was used to determine the mass of nicotine standards. The balance calibration was checked daily before use with three weights from a weight set that is calibrated annually. The three weights were selected to bracket the mass of the neat nicotine compound. The balance was rechecked with one calibration weight after use.

Results and Discussion

Table 1 summarizes the test conditions for both deionized water and Cincinnati tap water.

		Target Concentrations				
		Nicotine		Chlorine		Starting
Test ID	Matrix	(mg/L)	(mM)	(mg/L)	(mM)	рН
Tap Control 1	Chlorinated Tap	0	0	2	0.03	
Tap Control 2	Cincinnati Tap	5	0.03	0	0	
Tap 3	Chlorinated Tap	1.25	0.01	2	0.03	7.93
Tap 5	Chlorinated Tap	1.25	0.01	10	0.14	7.91
Tap 6	Chlorinated Tap	1.25	0.01	0.5	0.01	7.96
Tap 7	Chlorinated Tap	25	0.15	25	0.35	6.95
Tap 8	Chlorinated Tap	0.5	0	0.5	0.01	7.92
Nano Control 1	Nanopure Water, Buffered pH 7	5	0.03	0	0	6.92
Nano 2	Nanopure Water, Buffered pH 7	2	0.01	2	0.03	6.95
Nano 3	Nanopure Water, Buffered pH 7	1.25	0.01	4	0.06	6.92
Nano 4	Nanopure Water, Buffered pH 7	1.25	0.01	0.5	0.01	6.92
Nano 5	Nanopure Water, Buffered pH 7	0.5	0	0.5	0.01	6.93
Nano 6	Nanopure Water, Buffered pH 7	0.5	0	4	0.06	6.94
Nano 7	Nanopure Water, Buffered pH 7	25	0.15	25	0.35	7.00
Nano 8	Nanopure Water, Buffered pH 7	0.5	0	2	0.03	6.99
Nano 9	Nanopure Water, Buffered pH 7	1.25	0.01	2	0.03	7.00
Nano 10	Nanopure Water, Buffered pH 7	25	0.15	1	0.01	6.96

Table 1: Summary of test conditions

Figure 2 presents some of the test results.





Figure 2: Selected nicotine test results

As the figure indicates, both nicotine and free chlorine concentrations decreased significantly over time until they reached equilibrium. Each test scenario showed two-stage reaction kinetics, i.e., a rapid initial stage followed by a slower stage.

Nicotine and Chlorine Reaction Order and Reaction Rate Constants As mentioned above, the reaction between nicotine and chlorine exhibited a rapid initial reaction stage (Stage 1) followed by a slower reaction stage (Stage 2). Similar phenomena were observed by (Westerhoff et al., 2004) for the reaction between natural organic matter and free chlorine/bromine. Stage 1 lasted 1-3 minutes for nicotine. Initial nicotine or chlorine consumption was not caused by their reactions with other inorganics/organics present in solutions or glassware, as the control experiments (which omitted either nicotine or chlorine) showed no significant decrease in nicotine or chlorine concentrations. Therefore, high initial consumption of nicotine or chlorine shown in the experiments was most likely due to the reaction between nicotine and chlorine.

In water, free chlorine combines with water to form hypochlorous acid (HOCI) and hydrochloric acid (Sawyer et al., 1994).

$$Cl_2 + H_20 \rightarrow HOCl + H^+ + Cl^-$$

The hypochlorous acid formed is a weak acid and is poorly dissociated at pH levels below 6.

$$HOCI \rightarrow OCI^- + H^+ (pKa = 7.5)$$

The relative amounts of HOCl and OCl⁻ in solution as a function of pH are shown in Figure 3 (Sawyer et al., 1994). The pKa of hypochlorous acid is 7.5; at pH levels below 7.5, more HOCl exists in solution than OCl⁻, and vice versa at pH levels higher than 7.5.



Figure 3: Effect of pH on the distribution of hypochlorous acid and hypochlorite ion in water

Two different pH levels were investigated in this study: pH 7.1±0.1 for deionized water and pH 7.9-8.8 for tap water. Because of the significant effects that pH has on the chemistry of chlorine in water, the nicotine and chlorine reaction orders and rate constants were determined separately for the two different pH levels.

Due to fast reactions during Stage 1, rate constants could only be estimated from pseudo-zeroorder calculations using the observed data, i.e., calculations of change in nicotine concentration over a period of one minute: Δ [nicotine]_{1min} (Westerhoff et al., 2004). Table 2 summarizes the calculated pseudo-zero-order and pseudo-first-order rate constants.

Table 2: Pseudo zero order and pseudo first order rate constants for nicotine reaction with
free chlorine during the rapid initial reaction stage

Matrix	ID	Initial Free Chlorine Concentration (mM)	Pseudo-zero-order Change (Δ[nicotine] in mM ⁻¹)	Pseudo-first- order Rate Constant	Regression Coefficent
				K' (sec ⁻¹)	R ²
	Nano 1	0.0563	0.0171		
	Nano 2	0.008	0.0018		
	Nano 3	0.0479	0.0007		
	Nano 4	0.006	0.0011		
Deionized	Nano 5	0.0062	0.0034		
Water	Nano 6	0.0451	0.0035		
	Nano 7	0.2871	0.1105		
	Nano 8	0.0271	0.0009		
	Nano 9	0.0277	0.0029		
	Nano 10	0.0133	0.0026	0.0067	0.97

	Tap 2	0.0563	0.0367		
	Tap 3	0.0282	0.0075		
	Tap 4	0.0563	0.0197		
Tap Water ^a	Tap 5	-	-		
•	Tap 6	0.0061	0.0026		
	Tap 7	0.3134	0.2303		
	Tap 8	0.0057	0.0006	0.013	0.99

^aThe Tap 1 test was conducted before the experimental procedure was finalized. Therefore, the first sample was collected 30 minutes after the test began, which had consequently already passed Stage 1. Therefore, the Tap 1 data was not used for the rate constant calculation.

Pseudo-first-order rate constants were obtained by plotting the pseudo-zero-order constants as a function of initial free chlorine ([HOCI]_{Total} = [HOCI] + [OCI⁻]) for each test run. Figure 4 and Figure 5 present pseudo-first-order rate constants for nicotine reactions with chlorine during Stage 1 in deionized and tap water. The calculated pseudo-first-order rate constant k' is 0.0067 sec⁻¹ and 0.013 sec⁻¹ for deionized and tap water, respectively.



Figure 4: Pseudo first order rate constant (k') for nicotine reaction with chlorine during the rapid initial reaction stage in deionized water



Figure 5: Pseudo first order rate constant (k') for nicotine reaction with chlorine during the rapid initial reaction stage in tap water

The observed decrease in nicotine concentration in the presence of free chlorine during Stage 2 is initially assumed to be first order with respect to nicotine concentration. If linearity is observed when plotting $\ln([nicotine]/[nicotine]_0)$ versus time, then this assumption would be valid when free chlorine is present in excess. The slope of the regression line from such a plot yields the pseudo-first-order rate constant (k', sec⁻¹) as described by the following expression (Duirk and Collette, 2005; Laidler, 1965):

$$\ln \frac{[Nicotine]}{[Nicotine]0} = -k't$$

Figure 6 shows selected graphs of pseudo-first-order rate constants obtained from Stage 2 for deionized and tap water. The first-order rate coefficients were determined from regression line slopes.



Figure 6: Determination of pseudo first order rate constant (k') during the second reaction stage

Table 3 is a summary of pseudo-first-order rate constants during Stage 2. As can be seen in the table, regression coefficients (R²) ranged between 0.82 and 0.99 for deionized water and between 0.85 and 0.98 for tap water. As demonstrated by the high regression coefficients, nicotine exhibited first-order dependency with respect to itself in the presence of free chlorine.

Matrix	ID	Initial Free Chlorine Concentration (mM)	К', min ⁻¹	R ²	Pseudo-first- order Rate Constant	Regression Coefficient R ²
	Nano 1	0.0563	0.0683	0.93		
	Nano 2	0.008	0.0005	0.95		
	Nano 2	0.008	0.0235	0.87		
	Nano 3	0.0479	0.0595	0.82		
	Nano 4	0.006	0.0101	0.94		
Deionized	Nano 5	0.0062	0.0117	0.91	10	0.07
Water	Nano 6	0.0451	0.0346	0.94	10	0.97
	Nano 7	0.2871	0.0119	0.91		
	Nano 8	0.0271	0.1123	0.99		
	Nano 9	0.0277	0.0344	0.88		
	Nano 10	`0.0133	0.0045	0.99		

 Table 3: Pseudo zero order and pseudo first order rate constants for nicotine reaction with free chlorine during the second reaction stage

	Tap 2	0.0563	0.0097	0.86		
	Tap 3	0.0282	0.0057	0.92		
	Tap 4	0.0563	0.0049	0.85		
Tan Matara	Tap 5	0.1183	0.2155	0.97	NA	0.22
Tap water	Tap 6	0.0061	0.0051	0.87	NA	0.22
	Tap 7	0.3134	0.0078	0.97		
	Tap 8	0.0057	0.0041	0.91		
	Tap 9	0.1507	0.0621	0.98		

^aThe Tap 1 test was conducted before the experimental procedure was finalized. Therefore, the first sample was collected 30 minutes after the test began, which had consequently already passed Stage 1. Therefore, the Tap 1 data was not used for the rate constant calculation.

R, regression coefficient.

The pseudo-second-order rate constant (k, $M^{-1}sec^{-1}$) was determined by plotting the pseudofirst-order rate constant (k') versus the initial free chlorine concentration ([HOCI]_{Total}) for each test matrix. Since both species of free chlorine (HOCl and OCl⁻) are present, the decrease of nicotine in the presence of free chlorine can be described by the following expression:

$$\frac{d[Nicotine]}{dt} = -k'[Nicotine] = k[HOCl]Total[Nicotine]$$

Where $k' = k[HOCI]_{Total}$

Figures 7 and 8 show the pseudo-second-order rate constant for nicotine's reaction with chlorine during Stage 2 in deionized and tap water, respectively. As can be seen in Figure 7, k' increased linearly with an increase in free chlorine concentration for deionized water, and the calculated pseudo-second-order rate constant (k) is 18 M⁻¹sec⁻¹. A linear relationship was not established between k' and free chlorine concentration for tap water, as shown by the very low regression coefficient (R^2) (0.2208) in Figure 8. This is most likely due to interference from other contaminants in tap water. Therefore, second-order reaction assumptions are not valid for tap water. It was observed, however, that the pseudo-first-order rate constants did not change significantly with the change of free chlorine concentration, thus the reaction of nicotine with chlorine in tap water might follow first-order kinetics in Stage 2. The first-order rate constant ranged between 0.0041-0.0097 min⁻¹ (6.8 x 10⁻⁵ – 1.6 x 10⁻⁴ sec⁻¹) with the average of 0.0062 min⁻¹ (1.6 x 10⁻⁴ sec⁻¹), which is two orders of magnitude lower than Stage 1.



Figure 7: Determination of pseudo second order rate constant (k) for deionized water



Figure 8: Determination of pseudo second order rate constant for tap water

The half-life of nicotine was calculated using the following equations (Laidler - , 1965):

First order reaction $t_{1/2} = \frac{1}{k} * ln(2)$

Second order reaction $t_{1/2} = \frac{1}{(k) * [Nicotine]0}$

Table 4 presents a summary of the reaction order, rate constants, and half-life of nicotine at two reaction stages.

Test Matrix	Reaction Stage	Reaction Order	Reaction Rate Constant	Half-life of Nicotine (sec)
Deionized	1	First Order	0.0067 sec ⁻¹	103
Water	2	Second Order	18 M ⁻¹ sec ⁻¹	$\frac{1}{18[Nicotine]0}$ *
Тар	1	First Order	0.013 sec ⁻¹	53
Water	2	Second Order	1.6 x 10 ⁻⁴ sec ⁻¹	4332

Table 4: Reaction order, rate constants and half life for nicotine in chlorinated water

* [Nicotine]₀ is the initial nicotine concentration in moles/liter (M)

Nicotine and Chlorine Reaction Pathway Determination

Qualitative identification of intermediate compounds and byproducts from nicotine-chlorine reaction was performed via GC/MS. The identification of byproducts and intermediate compounds can assist with the identification of reaction mechanism and pathways between nicotine and chlorine. In addition, the intermediate compounds may be more toxic than the initial compound (nicotine in this case); therefore, it is important to identify the intermediate and final compounds.

Figure 9 presents a GC/MS chromatograph of a sample used to identify intermediate compounds produced by the nicotine-chlorine reaction.



Figure 9: Chromatograph of a sample to identify intermediate compounds by GC/MS

Table 5 summarized a list of intermediate compounds and byproducts identified by GC/MS.

Retention Time			_
(min)	Compound	Molecular Formula	Structure
17.65	Nicotine 3-(1-methyl-2- pyrrolidyl)pyridine	$C_{10}H_{14}N_2$	H ₃ C
18.741	Myosmine, 3-(pyrrolin-2- yl)pyridine	$C_9H_{10}N_2$	
19.405	5-methyl-4-phenyl- 1H-pyrazole	$C_{10}H_{10}N_2$	E C
19.70	Methyl-3-pyridyl- ketone	C7H7NO	
20.40	4-chloro-1-methyl- 1,2-dihydro-1,5- naphthyridin-2-one	C ₉ H ₇ ClN ₂ O	o v or
22.112	Cotinine, 1-methyl-5-(3- pyridyl)pyrrolidin-2- one	$C_{10}H_{12}N_2O$	N CH3

 Table 5: GC/MS identified intermediate compounds produced by the nicotine-chlorine reaction

Conclusions

Two-stage reaction kinetics were observed for the reaction of nicotine with free chlorine—a rapid initial stage followed by a slower reaction stage. The initial stage followed first-order reaction kinetics with a first-order rate constant k' of 0.0067 sec⁻¹ for deionized water, and 0.013 sec⁻¹ for tap water. For the slower reaction stage, the reaction followed second-order kinetics in deionized water with a second-order rate constant k of 18 M⁻¹sec⁻¹. In tap water, the reaction did not follow second-order kinetics, and the reaction order was estimated as first-order with a rate constant k' of 1.6 x 10⁻⁴ sec⁻¹, which was two orders of magnitude lower than the rapid initial reaction stage.

GC/MS proved to be a reliable and convenient way to identify reaction products. The following intermediate compounds were identified: myosmine, 5-methyl-4-phenyl-1H-pyrazole, methyl-3-pyridyl ketone, 4-chloro-1-methyl-1,2-dihydro-1,5-naphthyridin-2-one, and cotinine. Additional efforts are needed to identify and quantify dominant intermediate compounds to determine the mechanism of the nicotine-chlorine reaction.

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